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Derivation of Site-Specific Water Quality Criteria for Cadmium and the St. Louis River Basin, Duluth, Minnesota

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16. ABSTRACT

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The site-specific maximum concentration derived from the recalculation procedure was slightly lower (1.3 as compared with 2.2 μg/L) than the national criterion. The maximum concentration derived from the indicator species procedure was 7.0 μg/L and was calculated by using a water effect ratio from tests conducted in both site and laboratory water. Acute tests with several species demonstrated that cadmium was less toxic in site water than in laboratory water. The site-specific maximum concentration derived from the resident species procedure (from eight species exposed to cadmium in site water) was 1.9 μg/L. The 30-d average concentrations were the same as the maximum concentrations in the procedures in which the national acute/chronic ratio was used in the calculation. These concentrations were much lower when the site-specific acute/chronic ratio was applied.

Acute tests conducted monthly in site water showed that cadmium toxicity varied by more than a factor of 3 over the year. This indicates the need for considering seasonal changes in physical and chemical characteristics of the site water when deriving criteria to protect aquatic life.

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Hazard Assessment

DERIVATION OF SITE-SPECIFIC WATER QUALITY CRITERIA FOR CADMIUM AND THE ST. LOUIS RIVER BASIN, DULUTH, MINNESOTA

R. L. SPEHAR* and A. R. CARLSON

U.S. Environmental Protection Agency
Environmental Research Laboratory–Duluth
Duluth, Minnesota 55804

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Abstract — Several freshwater aquatic species were exposed to cadmium in site and laboratory water to evaluate a protocol recommended by the U.S. Environmental Protection Agency for deriving site-specific water quality criteria. The recalculation, indicator species and resident species procedures of this protocol were used to modify the national cadmium criteria. These procedures were used to account for differences in species sensitivity and in the biological availability and/or toxicity of cadmium due to physical and/or chemical characteristics of the site water.

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Keywords — Water quality criteria Toxicity Cadmium Freshwater aquatic organisms

INTRODUCTION

Under the Clean Water Act of 1977 [Section 304(a)(1)], the U.S. Environmental Protection Agency (EPA) is required to review and publish criteria for water quality necessary to protect public water supplies and the propagation of shellfish, fish and wildlife. The criteria present scientific data and guidance on the environmental effects of pollutants which can be useful to derive water quality-based regulatory requirements such as effluent limitations, water quality standards or toxic pollutant effluent standards [1].

National water quality criteria have been derived by applying a set of guidelines [2] to data for certain pollutants designated as toxic under Section 307(a)(1) of the Clean Water Act of 1977 pursuant to an agreement in the case of Natural Resources Defense Council et al. v. Train, 1976. These guidelines specify that criteria should be based on an array of data from species, both

*To whom correspondence may be addressed.

plant and animal, occupying various trophic levels. Based on these data, criteria can be derived that should adequately protect the types of species necessary to support an aquatic community. Although the criteria represent a reasonable estimate of pollutant concentrations consistent with the maintenance of designated uses, each state may modify these values to reflect local conditions.

Since national criteria may be either underprotective or overprotective, the U.S. EPA has developed guidelines [3] for modifying national water quality criteria to local conditions, i.e., site-specific criteria. National criteria are based on information obtained from toxicity and bioconcentration tests conducted in the laboratory. However, toxicological information obtained for laboratory-tested aquatic species may not be applicable to species in specific water bodies because (a) the species at a particular site may be more or less sensitive than those included in the national criteria database or (b) the physical and/or chemical characteristics of the water at the site may alter the biological availability and/or toxicity of the material.

The main purpose of this research was to test the recommended procedures for deriving site-specific water quality criteria [3]. The specific objective of the study was to conduct tests to evaluate these procedures utilizing toxicity tests with several species of aquatic organisms in site and laboratory water. The type of tests and/or exercises that were performed in this study were designed to correlate with the site-specific guidelines as they are now written. This study was designed to help identify problems that might be encountered when the guidelines are used and to provide an example for a site-specific criteria derivation for a chemical at an actual site.

Tests were conducted with cadmium because this chemical is highly toxic to aquatic organisms [4], is commonly found in the environment due to its presence in treated municipal wastes [5] and its chemistry in water is such that it may be influenced by changes in water quality [6–8], which would be a major consideration in modifying the present national criteria.

The St. Louis River system near Duluth, MN, was chosen as the site for study because water quality monitoring data and hydrodynamic and water quality models were available [9], because it contained clean water upstream of municipal and industrial discharges and because resident aquatic species for this river system were already known [10].

TERMINOLOGY

The following is an abbreviated list of definitions of terms that will be helpful in understanding the present procedures for deriving site-specific criteria for cadmium. A more complete list can be found in the national and site-specific guidelines for deriving water quality criteria [2,3].

Acute value. A 48- to 96-h LC_{50} or EC_{50}, depending on species.

Chronic value. Geometric mean of lower chronic limit (highest tested concentration in an acceptable chronic test that did not cause significant decreases from the control) and upper chronic limit (lowest tested concentration in an acceptable chronic test that caused significant decreases from the control).

Acute/chronic ratio. Ratio of an acute value for a species to a comparable chronic value for that species tested in the same water.

Final Acute Value (FAV). An estimate of the concentration of a material corresponding to a cumulative probability of 0.05 in the acute toxicity values for the families with which acute tests have been conducted for that material. (For an exception and the effects of water quality characteristics on this value, see ref. 2.)

Final Acute/Chronic Ratio. Geometric mean of all the species mean acute/chronic ratios available for both freshwater and saltwater species. (For variations in the calculation of this value, see ref. 2.)

Final Chronic Value (FCV). An estimate of the concentration of a material corresponding to a cumulative probability of 0.05 in the chronic toxicity values for families with which chronic tests have been conducted for that material, usually obtained by dividing the FAV by the Final Acute/Chronic Ratio. (For an exception and the effects of water quality characteristics on this value, see ref. 2.)

Criterion Maximum Concentration. FAV divided by 2.

Criterion (30-d) Average Concentration. The lowest of the criterion maximum concentration, FCV, Final Plant Value and Final Residue Value, unless other data from tests in which the concentrations of the test material were measured show that a lower value should be used. (For the effects of water quality characteristics on this value, see ref. 2.)

National criteria. To protect aquatic life and its uses, in each 30 consecutive days, the average concentration of a material should not exceed the Criterion Average Concentration; the maximum concentration should not exceed the Criterion Maximum Concentration; and the concentration may be between the Criterion Average Concentration and the Criterion Maximum Concentration for up to 96-h.

PROCEDURES AND TEST METHODS

Procedures for calculating criteria

The three procedures from the site-specific guidelines [3] were used in this study to modify the national Criterion Maximum and 30-d Average Concentration for cadmium. They were used for illustrative purposes only, because all three procedures would not necessarily be used in an actual site modification. The three procedures used to calculate the site-specific criteria for cadmium in the St. Louis River were as follows: (a) The *recalculation procedure* was used to account for differences in cadmium sensitivity between species resident in the St. Louis River and those species contained in the national cadmium criteria document [11]. (b) The *indicator species procedure* was used to account for differences in the biological availability and/or toxicity of cadmium due to physical and/or chemical characteristics of the St. Louis River water and laboratory water by deriving a water effect ratio (toxicity in site water divided by the toxicity in laboratory water). (c) The *resident species procedure* was used to account simultaneously for differences in both resident species sensitivity and differences that may be attributed to water quality.

In addition to the above procedures, acute tests were conducted on 1-d-old fathead minnows monthly to determine if seasonal changes in water quality affected the toxicity of cadmium in the St. Louis River.

Procedures to determine a Final Residue Value or a Final Plant Value (which are required in the national guidelines for deriving water quality criteria) [2] were not included in this study because cadmium is not a lipid-soluble material and plants have not been shown to be as sensitive to cadmium as are aquatic animals. Thus, the site-specific FCV for cadmium was the same as the site-specific 30-d average concentration for all procedures conducted in this study.

A detailed description of how to define a site, the rationale, assumptions and limitations of the site-specific procedures and their relationship to those used for deriving national water quality criteria are included in the recommended site-specific guidelines [3].

Water characteristics

The site chosen on the St. Louis River for the source of dilution water in this study was located approximately 34 miles upstream from the mouth of the Duluth–Superior estuary on the State Highway 33 crossing in the city of Cloquet, MN. Water samples were taken from the north channel to represent the river's quality immediately before the influence of the Cloquet area. This site on the river was considered to have the best

water quality closest to the impacted Duluth–Superior estuary (J. Stepun, personal communication). Water at this site was also judged to be of high quality because several species of aquatic organisms were able to survive, grow and reproduce in it under laboratory conditions with no apparent adverse effects. No industrial point discharges existed upstream of this site. Both reconstituted and Lake Superior water were used as laboratory dilution water in comparative toxicity tests. Reconstituted water was made according to procedures described by the American Society for Testing and Materials [12] for soft water. Unfiltered Lake Superior water was obtained directly from the lake. All waters were heated (if necessary) to the appropriate temperature for each test.

Chemical characteristics of the site water were determined after each collection by the Western Lake Superior Sanitary District located in Duluth, MN. In addition, chemical characteristics for all dilution waters were measured just prior to or during all toxicity tests at the Environmental Research Laboratory in Duluth, and were conducted according to procedures of the American Public Health Association [13]. Values for these measurements for tests conducted monthly with fathead minnows in each of the dilution waters are shown in Table 1. Water quality values for tests conducted with other species were within the range of the values shown.

Exposure systems

Static tests with larval fish were conducted in 600-ml glass beakers containing 500 ml of solution. Glass beakers containing 200 ml of solution were used for static tests with invertebrates. Wide-mouth glass jars containing 5 to 10 liters of test solution were used for static tests with juvenile fish. Duplicate test chambers were used in all tests for each of five toxicant concentrations and a control. All test chambers used for these tests were contained in a water bath for temperature control. Fluorescent light bulbs provided a light intensity of 80 to 100 lux during a 16-h photoperiod.

Flow-through acute and chronic exposures with fish were conducted using a diluter system [14] that delivered five toxicant concentrations and a control to four replicate chambers per treatment. Glass test chambers measured 7 cm wide × 19 cm long × 9 cm high, with a water depth of 4.5 cm. The flow to each chamber was 12.5 ± 1 ml/min. Fluorescent bulbs provided a light intensity of 200 to 500 lux at the water surface during a 16-h photoperiod.

Toxicant solution

Stock solutions for static tests were prepared by dissolving reagent-grade cadmium chloride ($CdCl_2$) in distilled water. Water samples were analyzed with a Perkin-Elmer atomic absorption spectrophotometer equipped with either an HGA 500 graphite furnace or an automatic burner control. The limits of detection for these procedures were approximately 0.25 and approximately 35 μg/L, respectively. All measurements are expressed as cadmium, not as cadmium chloride. To verify the accuracy of the method of analysis, known amounts of the metal were added to control water to obtain percentage recoveries. Percentage recoveries ranged from 91 to 110% for 76 spiked samples. In addition, one set of sample was periodically filtered through a 0.45 μm Millipore filter to characterize the proportion of dissolved metal. The mean percentages, standard deviation and number of samples of dissolved cadmium for individual tests (including five cadmium concentrations per test) were 84 ± 1.0 (n = 8), 84 ± 1.0 (n = 4) and 96 ± 2.0 (n = 9) for St. Louis River, Lake Superior and reconstituted water, respectively.

Biological procedures

Test species exposed to cadmium in this study are shown in Table 2. The sources of these species were provided in a more detailed description of this study [10]. Tests to

Table 1. Monthly averages in water quality parameters for cadmium tests with fathead minnows conducted in St. Louis River, reconstituted and Lake Superior water

Parameter	April	May	June	July	August	Sept	Oct	Nov	Dec
St. Louis River water									
Hardness	63.0	55.0	59.0	66.0	65.0	74.0	79.0	62.0	60.0
Acidity	2.9	2.6	4.0	2.3	4.2	3.6	2.0	2.9	3.7
Alkalinity	54.0	41.0	50.0	55.0	52.0	65.0	42.0	46.0	49.0
pH	7.6	7.2	7.4	7.6	7.3	7.8	7.6	7.3	7.4
Conductivity	146	104	134	138	155	165	115	129	132
TC[b]	—[a]	24.0	31.7	33.2	34.7	28.7	31.7	28.2	28.9
TIC[c]	—	7.5	12.7	11.1	11.7	14.2	10.3	10.1	9.9
DIC[d]	—	—	12.5	11.0	6.6	14.3	9.2	10.3	—
TOC[e]	—	16.5	19.0	22.2	23.0	14.6	21.4	18.1	19.0
DOC[f]	—	—	18.8	22.6	24.4	14.0	22.8	18.6	—
Turbidity	3.0	2.0	6.0	20.0	10.0	3.0	5.0	2.0	2.0
Color (CU)	120	150	190	230	210	180	280	195	120
Cl^-	6.5	5.0	4.0	4.5	5.0	5.5	6.0	5.0	5.0
SO_4^{2-}	11.0	10.0	9.0	10.0	15.0	12.0	12.0	18.0	13.0
Susp. Solids	6.8	2.8	9.2	27.0	14.4	0.4	0.4	0.4	1.2
Diss. Solids	97	104	104	142	147	144	114	136	125
Reconstituted water									
Hardness	40.0	48.0	41.0	42.0	41.0	39.0	—	—	—
Alkalinity	30.0	42.0	29.0	30.0	29.0	26.0	—	—	—
Acidity	—	2.1	2.3	1.9	5.7	4.1	—	—	—
pH	7.5	7.9	7.4	7.3	7.0	7.7	—	—	—
Conductivity	136	155	167	165	136	160	—	—	—
Lake Superior water									
Hardness	—	45.0	—	—	—	—	—	47.0	44.0
Alkalinity	—	40.0	—	—	—	—	—	42.0	41.0
Acidity	—	2.1	—	—	—	—	—	2.2	3.4
pH	—	7.4	—	—	—	—	—	7.4	7.4
Conductivity	—	100	—	—	—	—	—	95.0	93.0

[a]No measurement made.
[b]TC = Total carbon.
[c]TIC = Total inorganic carbon.
[d]DIC = Dissolved inorganic carbon.
[e]TOC = Total organic carbon.
[f]DOC = Dissolved organic carbone.

Table 2. Acute values (LC_{50}, μg/L) for juvenile aquatic species exposed to cadmium in St. Louis River and reconstituted water

Organism	Age (d) or weight (g)	Test temp (°C)	Endpoint	Exposure water	
				St. Louis River	Reconstituted
Cladoceran (*Daphnia magna*)	< 1 d	20	48 h	166 (124 - 221)[b]	—[a]
Cladoceran (*Ceriodaphnia reticulata*)	< 1 d	20	48 h	129 (104 - 160)	—
Cladoceran (*Simocephalus vetulus*)	< 1 d	20	48 h	89.3 (73.6 - 108)	—
Cladoceran (*Simocephalus serrulatus*)	< 1 d	20	48 h	123 (106 - 141)	24.5 (18.6 - 32.1)
Amphipod (*Gammarus pseudolimnaeus*)	0.1 g	17	96 h	54.4 (35.7 - 82.9)	68.3 (38.7 - 121)
Amphipod (*Hyalella azteca*)	0.001 g	7	96 h	285 (232 - 350)	—
Mayfly (*Paraleptophlebia praepedita*)	0.002 g	12	96 h	449 (166 - 1,217)	—
Rainbow trout (*Salmo gairdneri*)	0.5 g	12	96 h	10.2 (7.9 - 13.1)	2.3 (1.6 - 3.3)
Brown trout (*Salmo trutta*)	1–2 g	12	96 h	15.1 —[c]	1.4 (1.1 - 1.8)
Fathead minnow (*Pimephales promelas*)	30 d	25	96 h	3,390 (2,710 - 4,240)	1,280 (1,100 - 1,470)
Bluegill (*Lepomis macrochirus*)	0.7 g	17	96 h	8,810 (8,200 - 9,450)	—
Channel catfish (*Ictalurus punctatus*)	0.4 g	17	96 h	7,940 (7,080 - 8,910)	—

[a]No test was conducted.
[b]95% confidence limits.
[c]95% confidence limits could not be calculated using this method [17].

determine a water/effect ratio were conducted in both site and laboratory water with each species at the same time and under the same test conditions. Tests with different species were conducted throughout the year as they became available from their respective sources.

Tests were conducted monthly, beginning in April and ending in December 1981, to determine the effect of seasonality on the physical and chemical characteristics of the site water and the subsequent effects on biological availability, and for toxicity of cadmium on fathead minnows. These tests were conducted in site, reconstituted and/or Lake Superior water for 96 h for the calculation of LC_{50} values. Acute tests lasted for 96 h with other species, except for cladocerans whose tests lasted 48 h, and LC_{50} values were calculated as the response variable. All species, except cladocerans, were acclimated to the test water for at least 2 d prior to testing. Cladocerans were reared in the dilution water for a sufficient amount of time to produce young before being tested. Procedures for conducting acute tests followed those described by the American Society for Testing and Materials [12].

Chronic tests lasted for 32 d for fathead minnows and 9 d for cladocerans. These tests were done according to procedures described by the American Society for Testing and Materials [15] and Mount and Norberg [16], respectively. Survival, growth and/or reproduction were used as the response variables in these tests.

Statistical analysis

A computerized version of the modified, trimmed Spearman-Karber method described by Hamilton et al. [17] was used to determine 48- and 96-h LC_{50} values. Daily mortality data of replicate exposure tanks were combined before LC_{50} values were calculated.

For chronic tests, survival and embryo hatchability data were transformed to arcsin% [18] for variance stabilization. Individual weights from fish in replicate chambers were pooled before the data were subjected to a one-way analysis of variance ($p = 0.05$) and to Dunnett's one-sided comparison of treatment means to control means ($p = 0.05$) [19].

RESULTS AND DISCUSSION

No particular trend was observed for any water quality parameter measured for seasonality tests in St. Louis River, reconstituted and Lake Superior water. Most values were relatively constant [<25% relative standard deviation (RSD)]. Values for turbidity and suspended solids, however, were highly variable (100 and 129% RSD, respectively).

Monthly LC_{50} values for tests with 1-d-old fathead minnows exposed to cadmium in St. Louis River and reconstituted water are shown in Figure 1. Tests were not continued with reconstituted water during the months of November and December because of unexplained mortality of animals cultured in this water during October. Lake Superior water was used to replace reconstituted water as representative laboratory water. The mean acute value for cadmium obtained from tests in Lake Superior in November and December was 42 μg/L. Acute values calculated from exposures in river water varied by a factor of 3 and increased with increased suspended solids, total organic carbon, turbidity and dissolved solids concentration. Linear regression correlation coefficients for acute toxicity and these parameters were 0.58, 0.60, 0.68 and 0.77, respectively. The LC_{50} values for tests conducted in reconstituted and Lake Superior water varied by less than a factor of 2. The larger variation in values obtained from tests conducted in site water was attributed to high and low stream flows, which influenced water quality factors throughout the year. The large degree of binding or complexing of cadmium that occurred during times when concentrations of particulates in this water were highest was the apparent cause of reduced cadmium toxicity. Although this effect on toxicity was not large in the present tests, larger variations in toxicity may occur in streams where particulate loads change significantly during different times of the year. The frequency of testing needed to determine seasonal toxicity differences will depend on this variability. The frequency will have to coincide with the waste treatment facilities design flow or with National Pollutant Discharge Elimination System (NPDES) permits issuance.

Tests to determine seasonal differences (Fig. 1) showed that the average acute values for larval fathead minnows in St. Louis River water were approximately five and two times higher than those obtained in reconstituted and Lake Superior water, respectively. A similar toxicity difference was observed for four of five juvenile species exposed to these waters (Table 2). These findings indicate that physical and/or chemical characteristics of the St. Louis River water reduced the biological availability and/or toxicity of cadmium from that observed in laboratory water. This result confirms the basic assumption underlying the indicator species approach for criteria modification, which this study was designed to verify in a field situation. Although certain factors such as pH, hardness, alkalinity and carbon dioxide have been the most studied and quantified with respect to their effects on heavy metal toxicity, the literature indicates that organic solutes, inorganic and organic colloids and suspended particulates play a major role in affecting the toxicity of heavy

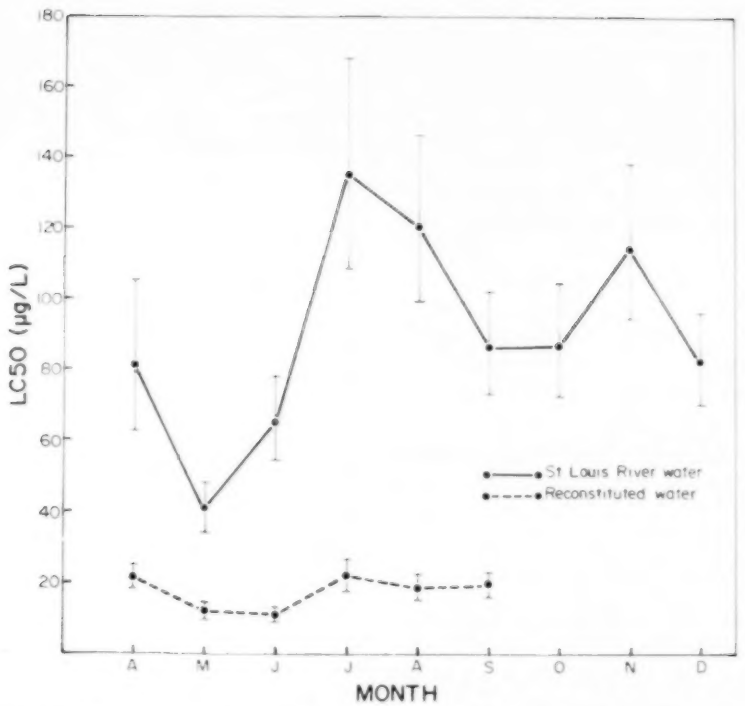

Fig. 1. Monthly LC_{50} values (± 95% confidence limits) for tests with 1-d-old fathead minnows exposed to cadmium in St. Louis River and reconstituted water.

metals to aquatic life (W. Spoor, unpublished manuscript). Recent work by D. A. Benoit (unpublished manuscript) has shown that hardness alone has relatively little effect on cadmium toxicity in Lake Superior water, but that suspended solids (clay) and dissolved solids (humic acid) greatly reduce cadmium toxicity to fathead minnows.

Results of 32-d early life stage tests with fathead minnows exposed to cadmium in St. Louis River water showed that survival was significantly reduced at 26.7 µg/L but not at lower concentrations by the end of the test. Growth was not decreased at any of the concentrations where fish survived. Based on these results, the upper chronic limit (lowest tested concentration that caused significant decreases from the control) for cadmium in St. Louis River water was 26.7 µg/L and the lower chronic limit (the highest tested concentrations that did not cause significant decreases from the control) was 13.4 µg/L. The chronic value (geometric mean of the chronic limits) [2] for this species was 18.9 µg/L. Chronic effects of cadmium on cladocerans (*Ceriodaphnia reticulata*) exposed in St. Louis River water indicated that survival was significantly reduced at 15.2 µg/L. By the end of the test, the next lower concentration of 7.2 µg/L reduced the mean number of young produced. Concentrations below 7.2 µg/L caused no significant adverse effect on this species after the 9-d test. The chronic value for this species based on the chronic limits of 3.4 to 7.2 µg/L calculated from these results was 4.9 µg/L. The chronic values estimated for both species exposed to cadmium in site water were similar to the values of 13 and 5.2 µg/L found for these species, respectively, by other investigators (D. A. Benoit and D. I. Mount, unpublished manuscripts) using laboratory (Lake Superior) water.

CRITERIA CALCULATION

Based on the results of the tests described above, site-specific water quality criteria for cadmium in the St. Louis River were derived using the following procedures [3].

Recalculation procedure

This procedure allows for modification of the national maximum concentration for cadmium [11] by eliminating data for non-resident species from the national database.

The data set for resident species in the St. Louis River was sufficient to meet the minimum data set requirements of the national guidelines [2] (Table 3). Thus, no additional acute tests in laboratory water were needed to calculate a site-specific criterion using this procedure. The site-specific FAV for this procedure and cadmium was calculated to be 2.4 μg/L for the data set using the procedure described in the national guidelines [2]. The site-specific maximum concentration was derived by the following equation: site-specific maximum concentration = site-specific FAV/2.

The value obtained from this equation is 1.2 μg/L. However, because the toxicity of cadmium has been related to the hardness of the water, this relationship was taken into account using the method described by the national guidelines to adjust for hardness before the site-specific maximum concentration was calculated (Table 3). The site-specific maximum concentration for cadmium from the above equation, adjusted for the hardness of the St. Louis River [~55 mg/L as $CaCO_3$ (the lowest hardness measured in this water over a year's time)] was 1.3 μg/L using the recalculation procedure.

The recalculation procedure does not require testing to determine a site-specific 30-d average concentration. A site-specific FCV can be derived from this procedure by dividing the site-specific FAV by the national acute/chronic ratio. Since the national Final Acute/Chronic Ratio for cadmium is 2.0 [11], the site-specific FCV for cadmium is the same as the site-specific maximum concentration, or 1.3 μg/L. Since a site-specific Final Residue Value or a Final Plant Value was not available, the site-specific 30-d average concentration for cadmium in St. Louis River, using the recalculation procedure, was 1.3 μg/L.

Indicator species procedure

This procedure is based on the determination of a water effect ratio to account for the differences in the toxicity of cadmium in St. Louis River and laboratory water due to physical and/or chemical characteristics of these waters. Although tests with only one fish and one invertebrate species were required for this procedure, a cladoceran (*S. serrulatus*), rainbow trout and fathead minnows were selected as indicator species to provide additional information for this exercise. Tests for each species were conducted in each water, at the same time and under similar test conditions. A water effect ratio was calculated as: water effect ratio = site water LC_{50}/lab water LC_{50}.

Measured LC_{50} values for a toxicant must be significantly different [3] in the two waters for this procedure to be valid. (If the values are not different, then the national maximum concentration is the site-specific maximum concentration.) The 96-h LC_{50} values for cladocerans, rainbow trout and fathead minnows were statistically different in both site and laboratory water (Table 4) and their water effect ratios were similar [3]. This allowed them to be used for the calculation of a site-specific, maximum concentration in the following equation: site-specific maximum concentration (7.0 μg/L) = geometric mean water effect ratio (3.9) × national maximum concentration (1.8 μg/L).

The national maximum concentration was adjusted for the hardness of the laboratory water (45 mg/L as $CaCO_3$) before the site-specific maximum concentration was calculated. The site-specific maximum concentration for cadmium for the St. Louis

Table 3. *Recalculation procedure:* minimum data set for cadmium from the national criterion document for resident species and families in the St. Louis River

Rank	Family	Family mean acute value (μg/L)	Organism	Species mean acute value (μg/L)
10	Bithyniidae	8,400	Snail (*Amnicola* sp.)	8,400
9	Centrarchidae	3,174	Bluegill (*Lepomis macrochirus*)	4,775
			Pumpkinseed (*Lepomis gibbosus*)	1,343
8	Ephemerellidae	2,319	Mayfly (*Ephemerella* sp.)	2,319
7	Cyprinidae	1,743	Goldfish (*Carassius auratus*)	8,397
			Common carp (*Cyprinus carpio*)	215
			Fathead minnow (*Pimephales promelas*)	2,080
6	Chironomidae	1,200	Midge (*Chironomus* sp.)	1,200
5	Anguillidae	734	American eel[a] (*Anguilla rostrata*)	734
4	Physidae	150	Snail (*Physa* sp.)	150
3	Gammaridae	70	Scud (*Gammarus* sp.)	70
2	Daphnidae	27.8	Cladoceran (*Daphnia pulex*)	40.4
			Cladoceran (*Simocephalus serrulatus*)	62.3
1	Salmonidae	5.1	Chinook salmon (*Oncorhynchus tshawytscha*)	4.9
			Rainbow trout (*Salmo gairdneri*)	3.9

[a]Uncommon species.

Site-specific final acute value = 2.4 μg/L (calculated for a hardness of 50 mg/L from site-specific family mean acute values).

Site-specific criterion maximum concentration = (2.4 μg/L)/2 = 1.2 μg/L (for a hardness of 50 mg/L).

ln (site-specific criterion maximum intercept) = ln (1.2) − [slope × ln (50)]
= 0.182 − 4.538 = −4.356

Site-specific criterion maximum concentration = e[1.16 [ln hardness] − 4.356]
= 1.3 μg/L adjusted for a hardness of 55 mg/L

River was 7.0 μg/L using the indicator species procedure.

The site-specific 30-d average concentration for the indicator species procedure can be derived using three optional methods [3]: (a) by calculation (no testing required) using the national acute/chronic ratio and applying it to the site-specific FAV; (b) by performing two acute and two chronic tests, which include tests with both a fish and an invertebrate species, conducted in site water and by applying the resulting acute/chronic ratio to

Table 4. *Indicator species procedure:* acute values (LC_{50}) for indicator species exposed to cadmium in St. Louis River and reconstituted water

Organism	St. Louis River water (μg/L)	Reconstituted water (μg/L)	Water effect[a] ratio
Cladoceran (*Simocephalus serrulatus*)	123	24.5	5.0
Rainbow trout (*Salmo gairdneri*)	10.2	2.3	4.4
Fathead minnow (*Pimephales promelas*)	3,390	1,280	2.6

[a]Geometric mean water effect ratio = 3.9.

the site-specific FAV; (c) by conducting chronic tests with both a fish and an invertebrate species in both site and laboratory water and by applying the chronic water effect ratio to the national FCV.

The site-specific 30-d average concentration from the indicator species procedure using the national acute/chronic ratio [method (a)] was the same as the site-specific maximum concentration of 7.0 μg/L. The following equation was used for the calculation: site-specific FCV = site-specific FAV/(National Final Acute/Chronic Ratio).

The site-specific 30-d average concentration using the site-specific acute/chronic ratio [method (b)] was calculated to be 0.3 μg/L, based on a geometric mean acute/chronic ratio of 50 (from present tests performed in the St. Louis River water; Table 5) and the following equation: site-specific FCV = site-specific FAV/(site-specific final acute/chronic ratio).

The site-specific chronic value was obtained for both of these methods using a site-specific FAV of 14 (twice the site-specific maximum concentration obtained from the indicator species procedure).

The site-specific 30-d average concentration using the chronic water effect ratio [method (c)] from studies for two species (fathead minnows and cladocerans) was determined to be 1.0 because the chronic values obtained from tests in site and laboratory water were not significantly different (the chronic limits overlapped) [3] (Table 6). Since the mean chronic water effect ratio was not different from 1.0, the site-specific FCV is the same as the national FCV adjusted for the hardness of the St. Louis River, or 2.2 μg/L using this method. (Although tests were not conducted specifically to obtain a site-specific chronic value using this third method, due to the time constraints of this study, comparisons were made between present chronic tests in St. Louis River water and recent tests conducted with the same species in Lake Superior water at the Environmental Research Laboratory–Duluth for use as an example of a chronic water effect ratio for this method. According to the site-specific guidelines [3], tests in both waters should be run at the same time, with organisms from the same population and under the same test conditions.)

Resident species procedure

This procedure allowed for modification of the cadmium national criteria on the basis of tests conducted in site water with a set of resident species of the St. Louis River (Table

Table 5. Acute (LC_{50}) and chronic values for aquatic organisms exposed to cadmium in St. Louis River water

Organism	Acute value (μg/L)	Chronic value (μg/L)	Acute/chronic ratio[a]
Fathead minnow (*Pimephales promelas*)	1,830	18.9	97
Cladoceran (*Ceriodaphnia reticulata*)	129	5.0	26

[a]Geometric mean acute/chronic ratio = 50.

Table 6. Chronic toxicity values of two species exposed to cadmium in St. Louis River and Lake Superior water

Organism	Chronic value (μg/L)		Chronic water effect ratio[a]
	St. Louis River water	L. Superior water	
Fathead minnow (*Pimephales promelas*)	18.9 (13 - 26)[b]	13[c] (9 - 18)	1.0
Cladoceran (*Ceriodaphnia reticulata*)	5.0 (3.4 - 7.2)	5.2[d] (3.6 - 7.5)	1.0

[a]Chronic water effect ratios are 1.0, since values in site and laboratory water are not different (chronic limits overlap).
[b]Chronic limits.
[c]Data from D. A. Benoit (unpublished manuscript).
[d]Data from D. I. Mount (unpublished manuscript).

7). Because the minimum data set requirements for resident species were met at the St. Louis River site, substitute families were not needed for testing under this procedure. Furthermore, a family in a phylum other than arthropoda or chordata (i.e., Rotifera, Annelida, Molluska, etc.) was not included in this data set because it was not a requirement of the national guidelines at the time these tests were conducted. The site-specific FAV calculated using the prescribed method for deriving an FAV [2] for resident species was 3.8 μg/L. The site-specific maximum concentration was calculated as: site-specific maximum concentration = site-specific FAV/2.

The resulting site-specific maximum concentration for cadmium using the resident species procedure was 1.9 μg/L.

The 30-d average concentrations for the resident species procedure were obtained by the same methods [(a) and (b)] described earlier under the indicator species procedure using 3.8 μg/L as the site-specific FAV. The site-specific FCVs for these methods were 1.9 and 0.1 μg/L, respectively. The third method should not be used to calculate a site-specific FCV using the resident species procedure [3].

Cadmium water quality criteria derived from the above site-specific procedures and from the national cadmium criterion document are provided in Table 8 for comparison.

Summary of criteria calculation

Comparison of cadmium water quality criteria derived from the national and site-specific procedures (Table 8) showed that criteria values varied depending upon the procedure used. Site-specific criteria derived from the recalculation procedure were slightly lower than those of the national criteria. The lower recalculated criteria were attributed to the smaller number of families (*N*) used to calculate the site-specific FAVs

Table 7. *Resident species procedure:* minimum data set of resident aquatic species exposed to cadmium in St. Louis River water[a]

Rank	Organism	LC_{50} (μg/L)
8	Bluegill (*Lepomis macrochirus*)	8,800
7	Channel catfish (*Ictalurus punctatus*)	7,900
6	Fathead minnow (*Pimephales promelas*)	3,390
5	Mayfly (*Paraleptophlebia praepedita*)	449
4	Amphipod (*Hyalella azteca*)	285
3	Cladoceran (*Simocephalus serrulatus*)	123
2	Amphipod (*Gammarus pseudolimnaeus*)	54.4
1	Rainbow trout (*Salmo gairdneri*)	10.2

[a]Site-specific final acute value for this resident species data set = 3.8.

Table 8. Cadmium water quality criteria derived from the national and site-specific procedures

Criterion derivation procedure	Number of families used	Maximum concentration (μg/L)	30-d average concentration (μg/L)	
National	21	2.2[a]	2.2[a]	
Site-specific				
Recalculation	10	1.3[a]	1.3[a]	
Indicator	21[b]	7.0[c]	7.0	(a)[d]
			0.3	(b)
			2.2[a]	(c)
Resident	8	1.9	1.9	(a)
			0.1	(b)

[a]Adjusted for a water hardness of the St. Louis River of 55 mg/L as $CaCO_3$.
[b]The national database containing 21 families was used in this calculation.
[c]A national criterion of 1.8 μg Cd/L [adjusted for a hardness of 45 mg/L hardness (as $CaCO_3$)] was used in this procedure.
[d]Letters in parentheses indicate optional methods used for calculating the site-specific 30-d average concentration (see text).

(10 as compared to 21) and because the same sensitive families were used in both procedures. The site-specific maximum concentration criterion obtained from this procedure will usually be lower than national value because as N decreases so does the FAV [2].

Site-specific criteria for cadmium derived from the indicator species procedure were higher than those derived from the national and the recalculation procedure. This was expected because criteria derived from this procedure were based on a water effect ratio attributed to site water characteristics that decreased the bioavailability and/or toxicity of cadmium. Cadmium was found to be less toxic to several species in St. Louis River water than in laboratory water.

The site-specific maximum concentration derived from the resident species procedure was slightly higher than the criterion derived from the recalculation procedure but was lower than that obtained from the indicator species procedure. This was also expected, and was attributed to the combination of the use of data from a limited database ($n = 8$) (which resulted in a lower criterion) and the use of site water tests (which raised the criterion due to the mitigating effects of the site water). In addition, the site-specific 30-d average concentration derived from the chronic water effect ratio method (the third method under the indicator species procedure) in the present example was the same as the national FCV (adjusted for the hardness of our laboratory water) because the mean chronic water effect ratio was not significantly different from 1.0. The low 30-d average concentration obtained from the second method for both the indicator and resident species procedures was attributed to the large site-specific acute/chronic ratio used in the calculation of the site-specific FCV. The large site-specific acute/chronic ratio of 50 determined from the present tests was obtained for fathead minnows and cladocerans, which were different from the species used to calculate the national final acute/chronic ratio of 2.0. The small acute/chronic ratio used in the national water quality criteria document for cadmium [11] was determined for chinook salmon. Because the FAV and the FCV for cadmium were based on rainbow trout in the national document (a species in the same family as the chinook salmon), higher ratios were not used.

OVERALL ASSESSMENT

Although all the procedures from the site-specific guidelines [3] were tested in this study, only one of these approaches would probably be used in an actual site criteria

modification. If species sensitivity was the important factor, for example, where species at a particular site are more or less sensitive than those used to derive the national criteria, then the recalculation procedure would be the recommended approach because it would require no testing. When water quality at a site may mitigate the toxicity of a chemical and the resident species are similar to those used to calculate the national criteria, the indicator species procedure would be appropriate. This is especially true for metals like cadmium, for which biological availability and/or toxicity are significantly effected by variations in water quality characteristics of the site water. When both species sensitivity and water quality are important considerations for a particular site, the resident species procedure would be the best approach because it is designed to account for differences due to both of these factors.

For the St. Louis River Basin, the indicator species procedure would be the recommended approach for deriving site-specific criteria for cadmium. The present study showed that cadmium was less toxic in site water than in laboratory water, which resulted in a water effect ratio. This ratio was designed to account for water quality effects, and its use with the national maximum criterion concentration should provide a site-specific maximum criterion concentration that would adequately protect the resident aquatic species at this site. The recalculation procedure would not be appropriate in this case because there was no real difference between the sensitivity range of species represented in the national data set and species found at this site. This rationale would also apply to the resident species procedure, which in part accounts for species sensitivity. The resident species procedure could be used for this site but additional testing in site water would be required.

The site-specific 30-d average concentration can be obtained using three optional methods, described under the indicator species procedure above. However, the first method, which uses the national final acute/chronic ratio, may not be used at this particular site if professional judgment determined that certain sensitive species may not be protected by this site-specific criterion. For example, cadmium is a special case, in which the national 30-d average concentration was based on a small acute/chronic ratio from tests with salmonids. This criterion was derived to protect these organisms because they are sensitive to cadmium and are economically important species. However, daphnids were found to be even more sensitive to this chemical on a chronic basis. Because the first method uses the national acute/chronic ratio in this calculation, the site-specific 30-d average concentration of 7.0 μg/L (Table 8) may be too high to protect daphnids, which are numerous in the lower St. Louis River. The second method resulted in a much lower site-specific 30-d average concentration, based on actual testing with daphnids in site water, and would provide daphnid protection. The third method resulted in a criterion that was lower than the first but higher than the second. Although this is a valid method, the actual criterion value obtained for this site would not be used because tests were not done strictly in accordance with the site-specific guidelines and this method was only included to provide an example for this exercise.

The above procedures were designed for the derivation of site-specific water quality criteria by allowing substantial flexibility with respect to the method used. This should permit regulatory agencies to choose the most appropriate and efficient means of obtaining the information needed to modify national criteria for each particular site. Site-specific water quality criteria for cadmium and the St. Louis River obtained from the site-specific guidelines appear to be logical, as they take into account the national cadmium criteria and physical, chemical and biological characteristics of this site water. The use of these procedures to derive

site-specific water quality criteria for toxic materials at different sites should provide additional input for the development of effective site-specific guidelines.

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